

# Advances in Polymer Precursors and Bio-based Polymers Synthesized from 5-hydroxymethylfurfural

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## ABSTRACT

In recent years, considerable efforts have been made regarding the synthesis of renewable chemicals from natural resources. 5-hydroxymethylfurfural (HMF) is an interesting platform chemical which has been widely exploited due to its rich chemistry and potential availability. The versatility of HMF has been demonstrated in several areas such as fine chemicals, biofuel precursors and polymers. In particular, the potential to replace petroleum-based analogues in the preparation of polymers associated with high performance has been observed owing to the structural rigidity of furan rings. This review aims at critically discuss the current research studies related to the derivatives of HMF, alongside with the synthesis and characterization of (co-) polymers derived from HMF and its derivatives.

**KEYWORDS:** 5-Hydroxymethylfurfural; 2,5-Furandicarboxylic acid; Furan Derivatives; Bio-based Polymers;

## INTRODUCTION

The interest in polymers synthesized from renewable resources has been growing due to issues related to the environment, as well as the concerns about the potential depletion of petroleum resources. Therefore, a variety of natural macromolecules and renewable monomers, such as polysaccharides, lignin, succinic acid, vegetable oils, terpenes, and furan-based derivatives, have emerged in the preparation of various polymers.<sup>1-9</sup> 5-hydroxymethylfurfural (HMF) is a promising platform chemical owing to its sustainability and functional groups available for further reactions. Due to the importance of HMF, research works have focused on several key aspects: (1) biological properties, such as the metabolism of HMF and toxicological effects;<sup>10-13</sup> (2) synthesis of HMF including the catalysts used,<sup>14-21</sup> the feedstocks used,<sup>22,23</sup> and the solvent

systems;<sup>19,24-27</sup> (3) derivatives of HMF as biofuels precursors,<sup>28,29</sup> fine chemicals,<sup>30</sup> monomers for polymers,<sup>6,30-34</sup> and (4) industrial production of HMF and its derivatives.<sup>23,32,35</sup>

One of the most important applications of HMF is to synthesize monomers for polymers, such as 2,5-furandicarboxylic acid (FDCA) and 2,5-bis(hydroxymethyl) furan (BHF). In addition to the synthesis of FDCA-based polyesters, their physical properties (i.e. crystallinity, thermal and mechanical properties, thermal degradation, structural properties and permeability) have been investigated as well. The thermal and barrier properties of polyethylene 2,5-furandicarboxylate (PEF) were highly comparable to their analogue polyethylene terephthalate (PET).<sup>36-46</sup> More recently, catalytic production of FDCA from lignocellulosic biomass,<sup>47</sup> and FDCA-based polyesters and polyamides have been reviewed.<sup>48,49</sup> However,

other HMF derivatives, such as BHF and 2,5-diformylfuran (DFF) should be emphasized as well,<sup>10</sup> especially in combination with Diels-Alder reactions to prepare cross-linked or functional polymers.<sup>34,50-53</sup> Therefore, the aim of this review is to combine and condense the body of researches performed on the synthesis of HMF derivatives, the synthesis and the characterization of (co)-polymers from HMF and derivatives. Furthermore, future work to this field has also been suggested.

## BIO-BASED FURANS MONOMERS AND DERIVATIVES

The chemical structure of HMF comprises of a furan ring, a hydroxyl group and a formyl group, which are available for reduction, oxidation, esterification, or other reactions leading to useful target molecules. In this section, a variety of derivatives which may be or have been utilized in the areas of polymer science and engineering are presented. Note that details related to their synthesis can be found in other reviews and scientific publications.<sup>10,11,23,30,52</sup>

### Symmetrically Functional Derivatives of HMF

Due to the presence of functional groups on opposite sides of the heterocyclic ring of HMF, the preparation of symmetrically functional monomers is possible. Figure 1 summarizes a number of versatile monomers obtained by oxidation, reduction and derivatization of HMF. The following paragraphs will discuss these monomers which have been used in the synthesis of polyesters, polyurethanes and thermoset resins.<sup>52</sup>

The oxidation of hydroxyl and formyl groups of HMF to FDCA (12) can be performed via aerobic oxidation with Pt catalysts supported on TiO<sub>2</sub> and ZrO<sub>2</sub>,<sup>54</sup> RuO<sub>2</sub> catalysts with Mg-based supports,<sup>55</sup> magnetic Pd catalysts,<sup>56</sup> Ru/C catalyst,<sup>57</sup> as well as Au catalysts with a variety of supports.<sup>58-61</sup> Enzyme-catalyzed oxidation and a whole-cell biotransformation of HMF to (12) have also been performed.<sup>62,63</sup> Diesters (13) have been synthesized via the esterification of (12)

with corresponding alcohols.<sup>64,65</sup> Direct oxidative esterification of HMF to dimethyl 2,5-furandicarboxylate (13, R=methyl) was achieved using Au-ZrO<sub>2</sub> and Au-CeO<sub>2</sub> catalysts, respectively.<sup>66-68</sup> These monomers are valuable polyester precursors. Reaction of (12) and SOCl<sub>2</sub> in DMF afforded 2,5-furandiarbonyl chloride (16),<sup>69,70</sup> which was used in the synthesis of polyesters and polyamides.<sup>71</sup> Moreover, the addition of sodium azide in a solution of (16) yielded 2,5-dicarbazidofuran (17), which was further converted to diisocyanatofuran (18). Like other diisocyanates, (18) must be stored in an inert atmosphere due to its susceptibility to moisture.<sup>72,73</sup> Other derivatives of (12), such as diglycidyl ester of 2,5-furandicarboxylic acid (15) and bis(prop-2-enyl)furan-2,5-dicarboxylate (14) have been synthesized.<sup>74</sup> The use of (15) for the synthesis of bio-based epoxy resins showed promising results in terms of higher curing activity, elevated glass transition temperature (T<sub>g</sub>), as well as similar mechanical properties as compared to diglycidyl ester of terephthalic acid.<sup>74</sup>

BHF (5) is another valuable building block chemical. The acylation of the hydroxyl groups of (5) with acryloyl chloride using trimethylamine as catalyst yielded 2,5-furan diacrylate (6). The addition of (6) as a difunctional cross-linker through photo-polymerization increased the tensile strength of acrylated epoxidized vegetable oils based polymer networks by up to 4.2 times as compared with those without addition of (6).<sup>75</sup> Moreover, (6) has been used as a monomer for the synthesis of side-chain functional polyesters via the Baylis-Hillman reaction.<sup>76</sup> Reaction of (5) with allyl bromide produced 2,5-bis-allyloxymethyl-furan (7), which was utilized to prepare heteromacrocycles by ring-closing metathesis.<sup>77</sup> The synthesis of 2,5-bis[(2-oxiranylmethoxy)methyl]-furan (8) was performed by reaction of (5) with epichlorohydrin using tetrabutylammonium hydrogen sulfate as the catalyst. (8) has been utilized to prepare high-performance epoxies.<sup>78,79</sup> 2,5-bis(chloromethyl)furan (9) was synthesized by reacting (5) with SOCl<sub>2</sub> and

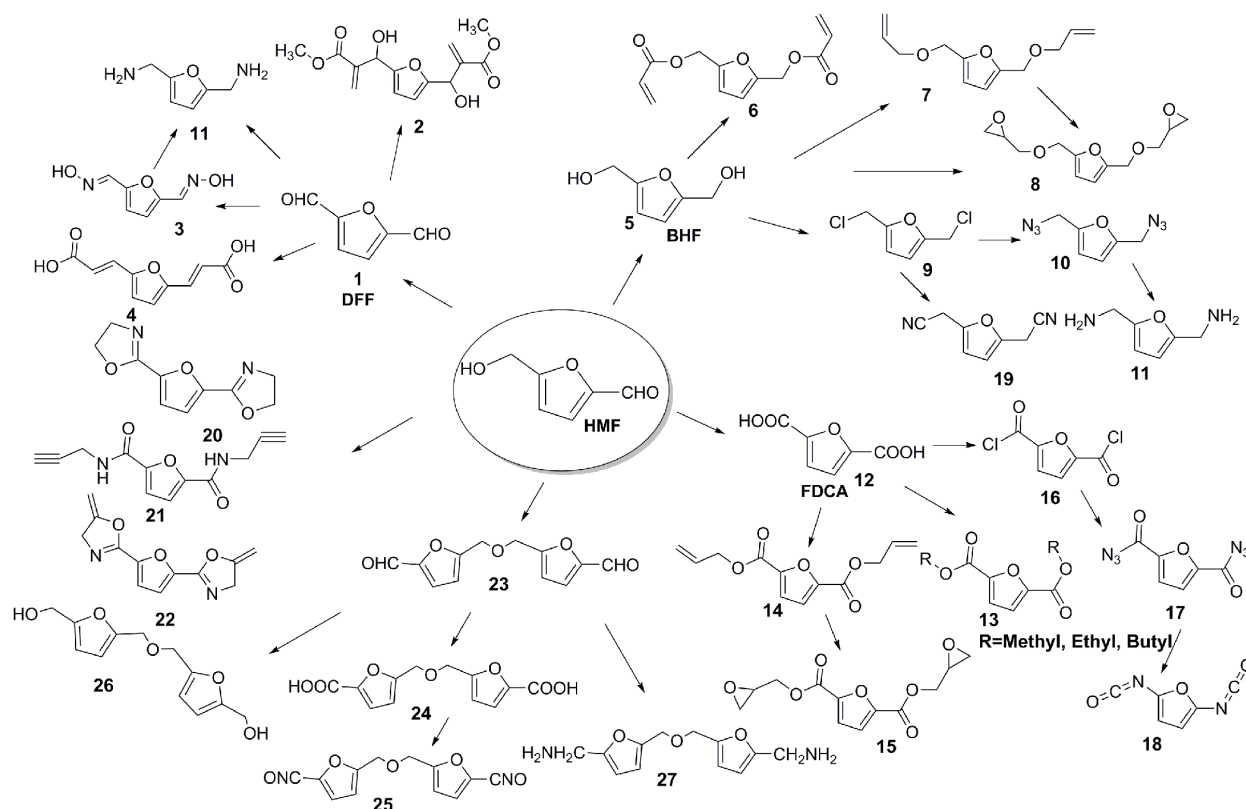


FIGURE 1 Symmetrically Functional Derivatives of HMF

pyridine in  $\text{CHCl}_3$  at  $-10\text{ }^\circ\text{C}$ .<sup>80,81</sup> Furthermore, (9) has been used to obtain 2,5-bis(azidomethyl)furan (10) and 2,5-bis(cyanomethyl)furan (19).<sup>81,82</sup> 2,5-bis(aminomethyl)furan (11), a building block for polyamides, can be synthesized by several approaches. Using Raney nickel as a catalyst, (11) was obtained by stirring a solution of (10) at 1 atm of  $\text{H}_2$  at room temperature for 40 h.<sup>81</sup> It can also be synthesized from DFF (1) with furan-2,5-dicarbaldehyde dioximes (3) as the intermediate.<sup>83</sup> Recently, (11) was prepared by the direct reductive amination of (1) with ammonia in one step. The use of acid treated Raney-Ni catalysts in combination with a THF-water medium was of importance because of its ability to suppress side reactions, leading to a relatively high yield (46 %).<sup>84</sup>

Additionally, 2,5-furandiacyrylic acid (4), a photo-responsive monomer, was synthesized from (1) using an excess of malonic acid and pyridine.<sup>85</sup> The photocyclodimerization of (4) was a

reversible process. Irradiation with a tungsten bulb led to the formation of dimers. The thermal decomposition of dimers to (4) occurred at  $220\text{ }^\circ\text{C}$ .<sup>85</sup> Dialdehyde groups of (1) were also available for the Baylis-Hillman reaction. Therefore, reaction of (1) with methyl acrylate using 1,4-diazabicyclo[2.2.2]octane (DABCO) as a catalyst generated (2).<sup>86</sup>

Li *et al.* described a facile and efficient method to synthesize 2,5-bis(4,5-dihydrooxazol-2-yl)furan (20) via reaction of (12) with  $\beta$ -amino alcohols in toluene for 24 h.<sup>87</sup> Recently, bio-based thermosets obtained through the polymerization of (20) with sebacic acid were prepared and characterized.<sup>88</sup> Other derivatives, such as N,N-di(prop-2-ynyl)furan-2,5-dicarboxamide (21) and 2,2'-furan-2,5-diylbis(5-methylene-4,5-dihydro-1,3-oxazole) (22), have been prepared as well.<sup>89,90</sup> They might be employed to synthesize polymers via radical polymerization or azide-alkyne reactions.<sup>91</sup> 5,5'-(oxydimethylene)-di-2-furaldehyde (23) used for

the synthesis of polyurethane foams was obtained via etherification of HMF catalyzed by several different catalysts, such as graphene oxide, homogeneous organic acids, and molecular sieves with Brønsted and Lewis acid sites.<sup>92-95</sup> Other approaches, such as the thermal dehydration of HMF in the presence of dimethylsulfoxide,<sup>96</sup> and the Williamson reactions between HMF and 5-chloro-methyl-2-furfural with an excess of base, have been used for the synthesis of (23) as well.<sup>97</sup> Dialdehyde groups of (23) can be further oxidized to dicarboxylic acids (24) using silver oxide in basic condition.<sup>94</sup> The conversion of (24) to diisocyanates (25) was accomplished in two steps using diazides as the intermediates.<sup>92</sup> Derivatives from (23), such as diols (26)<sup>98</sup> and diamines (27) have also been prepared.<sup>99</sup>

In addition to the derivatives mentioned above, continuous efforts are being put into upgrading HMF. Recently, Chen *et al.* have prepared a monomer, 5,5'-dihydroxymethyl furoin (DHMF) from the HMF in 95% yield via organocatalysis. Selective oxidation and reduction of DHMF afforded diol and tetraol monomers which were utilized in the synthesis of linear or cross-linked polyurethanes.<sup>100</sup> The synthesis of bis(hydroxymethylfurfural)amine from HMF has also recently been reported by reacting HMF with primary amines in the presence of homogeneous catalysts. These new monomers offer great potentials to form functional biopolymers with tunable properties.<sup>101</sup>

### Unsymmetrically Functional Derivatives of HMF

Figure 2 shows the derivatives of HMF prepared by selectively reacting hydroxyl or formyl groups of HMF. HMF can be efficiently converted to 5-hydroxymethyl-2-vinylfuran (28) by the Wittig reaction. This derivative is a good candidate for radical polymerization initiated by azobisisobutyronitrile.<sup>102</sup> The conversion of HMF to 5-(hydroxymethyl)furan-2-carbonitrile (29) can be accomplished using iodine in an aqueous ammonia solution.<sup>103</sup> 5-hydroxymethyl-2-furancarboxylic acid (30) has been prepared via the selective oxidation of aldehyde group to

carboxylic acid through a whole-cell biotransformation (*Serratia liquefaciens* strain),<sup>104</sup> or a heterogeneous catalyst prepared by immobilization of [MoO<sub>2</sub>(acac)<sub>2</sub>] on montmorillonite K-10 clays.<sup>105</sup> In addition, HMF has been selectively carbonylated to 5-formylfuran-2-acetic acid (31) in an acidic aqueous medium using Pd complex of trisulfonated triphenylphosphine as the catalyst.<sup>106</sup> The transformation of HMF to 1,3-dioxolane-4-methanol, 2-[5-(hydroxymethyl)-2-furanyl] (32) can be catalyzed by molybdenum and tungsten promoted SnO<sub>2</sub> solid acids.<sup>107</sup> Bio-based acrylate (33) has been synthesized by the Baylis-Hillman reaction of methyl acrylate with HMF.<sup>76,108</sup> The reaction of the hydroxyl group with acryloyl chloride gave 5-hydroxymethylfurfuryl acrylate (34).<sup>76</sup>

### Derivatives of HMF from Furan Ring Reactions

Most chemicals derived from the reaction of furan rings can be considered as potential biofuels candidates or precursors.<sup>109</sup> However, some derivatives have been utilized for the synthesis of polymers (Fig. 3). For the furan rings, a variety of reactions have been observed, such as reactions with electrophiles, nucleophiles, oxidants, reductants, cycloaddition, as well as metals and metallic derivatives.<sup>110</sup> Oxidation of the furan ring of HMF to (35) was performed in

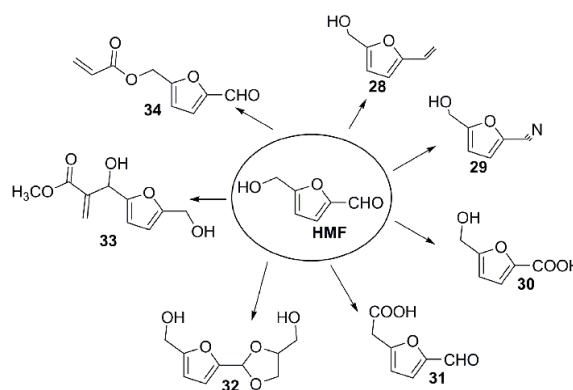


FIGURE 2 Unsymmetrically Functional Derivatives of HMF

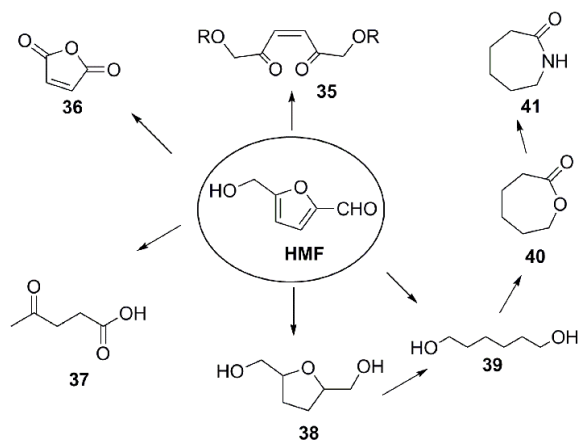


FIGURE 3 Derivatives of HMF via Furan Ring Reactions

two steps using meta-chloroperoxybenzoic acid as the oxidant.<sup>111</sup> Maleic anhydride (36), a versatile chemical intermediate, has been produced from HMF via oxidation with molecular oxygen using  $\text{VO}(\text{acac})_2$  as a catalyst.<sup>112</sup> Acid catalyzed decomposition of HMF generated levulinic acid (37). The properties and potential applications of levulinic acid have been reviewed.<sup>23,113</sup> Catalytic hydrogenation of HMF gave 2,5-tetrahydrofuran dimethanol (38) in a quantitative yield using a Ra-Ni catalyst at 100 °C.<sup>114,115</sup> 1,6-hexanediol (39) can be prepared via different routes, such as direct hydrogenation of HMF with a mixture of copper chromite and Pd/C as catalysts, and a two-step approach via (38) using Rh-Re/SiO<sub>2</sub> as a catalyst.<sup>116</sup> Recently, the direct production of (39) from HMF was achieved over a reusable Pd/zirconium phosphate catalyst at 140 °C using formic acid as a hydrogen source.<sup>117</sup> Further preparation of caprolactone (40) was successful in methyl isobutyl ketone at the reflux temperature for 30 mins, using the catalyst made *in situ*.<sup>116</sup> Conversion of (40) into caprolactam (41) by the reaction with ammonia was straightforward and has been well-established.<sup>118</sup> Last but not least, the Diels-Alder reaction between furan rings and maleimides, particularly for furfural and its derivatives, has been recognized as a versatile “click tool” in the macromolecular synthesis.<sup>119</sup> In the case of HMF and its derivatives, the effect of substitutions connected to the furan ring should be

considered in the design of monomers through Diels-Alder reactions, since those substitutions significantly influenced the reactivity between the furan derivatives and the maleimide derivatives.<sup>120</sup> For example, FDCA, an oxidation product of HMF, has been utilized to synthesize furan polyesters. However, the electron-withdrawing effect of the carbonyl groups connected to the furan ring prevented the Diels-Alder reaction of furan rings with maleimide.

In summary, a variety of HMF derivatives have been presented in the literatures. However, the problems in the synthesis of HMF derivatives still exist, such as low yield, high cost and high energy input. Thus, efforts to synthesize these derivatives in an economically feasible and environmentally friendly way are still needed. In addition, information about some of the HMF derivatives which can potentially be used in the synthesis of polymers is still missing. It deserves to be further investigated due to the renewability of HMF and unique properties of furan rings (diene). Moreover, the synthesis of new HMF derivatives could increase the utilization of HMF in the polymer field.<sup>100</sup>

## POLYMERS DERIVED FROM HMF AND ITS DERIVATIVES

The interest in polymers derived from HMF and its derivatives has been rapidly increasing not only due to the sustainability and rich chemistry of HMF, but also due to the unique properties of these polymers. Currently, the preparation of HMF derivatives based polymers are mainly performed via chemical approaches.<sup>33,121-123</sup> Enzymatic catalysis routes have been recently evaluated as well.<sup>53</sup> Therefore, in this section, the synthesis and characterization of polymers via chemical methods will be reviewed, starting from three key monomers (FDCA, BHF and DFF).

### Chemical Polymerization

#### *Polymers from FDCA and Its Derivatives*

Due to the presence of two carboxylic acid groups, FDCA and its derivatives have been

utilized in the synthesis of (co)polyesters, polyamides and other interesting polymers. Researches on (co)polyesters have been growing quickly in terms of synthesis, structural analysis, determination of the physical properties, as well as the sorption behavior with water, oxygen and carbon dioxide. Among FDCA based polyesters, poly(ethylene-2,5-furandicarboxylate) (PEF) and poly(butylene-2,5-furandicarboxylate) (PBF) are the most comprehensively studied due to their resemblance to the engineering plastic polyethylene terephthalate (PET) and polybutylene terephthalate (PBT). Poly(propylene-2,5-furandicarboxylate) (PPF) as the replacement of poly(propylene-2,5-terephthalate) (PPT) has also been investigated in terms of thermal behavior, solid state structure and barrier properties.<sup>124</sup> Besides these, varieties of other monomers, such as longer aliphatic linear diols, aromatic diols and renewable aliphatic acids, have been used to prepare (co)polyesters.<sup>125</sup>

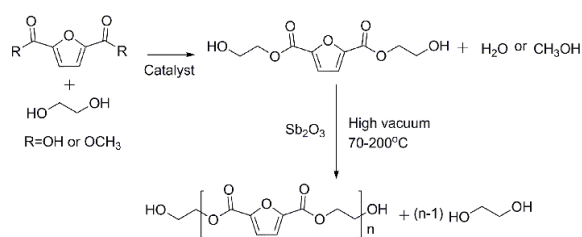
#### *Poly(ethylene-2,5-furandicarboxylate)*

Being entirely prepared from renewable FDCA and ethylene glycol (EG), PEF has been proposed as an important alternative for PET.<sup>48,126</sup> More importantly, it presents high performance in terms of thermal stability, mechanical and barrier properties.

Recently, a detailed description of PEF synthesis via two stage melting polymerization has been presented (Scheme 1).<sup>38,127</sup> The starting materials, reaction temperatures and catalysts have been suggested to influence the polymerization process and the polymer properties. The preferable starting monomer used for the polymerization reactions was dimethyl ester 2,5-furandicarboxylate (DMFD), rather than FDCA, in order to prevent the decarboxylation of FDCA. A high polymerization temperature (over 250 °C) was not recommended due to the color issue and a lower yield. In addition, tin (IV)/tin (II) catalyst system contributed to the increase in molecular weights. This approach seems to be effective, and has been widely adopted. However, issues still exist,

such as a long reaction time (hours to days) required to attain high reaction extents, and poor mass and heat transfer when the melt viscosity was high. Other synthesis routes, such as direct esterification using tetrabutyl titanate as a catalyst,<sup>127</sup> ring opening polymerization of cyclic FDCA based monomers,<sup>128</sup> and the combination of melting polymerization and subsequent solid state post condensation,<sup>129</sup> have also been presented. For the ring opening polymerization, although PEF with weight-average molecular weight between 50,000 and 60,000 g/mol has been synthesized,<sup>128</sup> the complicated process for the preparation of cyclic monomer and relatively low yield might limit its application.

The structure of PEF prepared via two stage melting polymerization was found to be semi-crystalline. The  $T_g$  and melting point ( $T_m$ ) were in the range of 75-80 °C and 210-215 °C, respectively.<sup>126</sup> PEF was thermally stable up to 300 °C. These behaviors were similar to those of PET, although PEF showed a relatively lower thermal stability. The density of amorphous PEF (1.43 g/cc) was higher than the density of amorphous PET (1.33 g/cc).<sup>36</sup> On the other hand, the differential scanning calorimetry (DSC) curves showed the absence of cold-crystallization and subsequent melting peak for amorphous PEF during the first heat cycle as compared to a significant cold-crystallization and melting peak for PET. This observation indicated a long time-scale for the crystallization process in PEF, probably due to the structural rigidity and the nonlinear axis of rotation around the furan ring.<sup>36</sup> However, Bikiaris *et al.* observed a cold-crystallization peak and subsequent melting



SCHEME 1 Synthesis of Poly(ethylene 2,5-furandicarboxylate)<sup>126</sup>

peak of melt-quenched PEF in the non-isothermal cold-crystallization experiment.<sup>37</sup> Furthermore, it showed that the cold crystallization temperature ( $T_{cc}$ ) increased with the increase of heating rates in the DSC analysis. The melting points were higher at slower rates due to the increased crystal stability. For PET, melting points were less affected by the different heating rates, and cold crystallization peaks were always located in about the middle of the range between  $T_g$  and  $T_m$ . From cold-crystallization studies and  $T_{cc}$ - $T_g$  differences, it was suggested that PEF chains were much less flexible than those of PET. Additionally, isothermal crystallization from the melt revealed multiple melting peaks for each PEF samples crystallized at different temperatures. The intensity and position of the peaks also varied in each PEF sample. It was suggested that two populations of lamellae of different stabilities, rather than recrystallization, might have contributed to these multiple melting behavior of PEF. Furthermore, wide-angle X-ray scattering (WAXS) study of each PEF samples showed similar peak patterns. It indicated that melting of crystals of different forms generated during the process of isothermal crystallization failed to explain the different melting behavior in each PEF samples.<sup>37</sup> Es *et al.* also observed multiple melting transitions for a high  $M_w$  PEF from DSC analysis obtained after isothermal crystallization at various temperatures (150 to 200 °C), but they believed that the multiple melting behavior was the result of melting and recrystallization of imperfect crystals.<sup>129</sup>

More recently, the Avrami equation was used to describe the isothermal crystallization kinetics of PEF. The Avrami exponent ( $n$ ) values were in the range of 2.2-2.6.<sup>37</sup> In addition, the maximum growth rate calculated with obtained Hoffman-Lauritzen parameters was  $T_{c,max} = 167$  °C.<sup>130</sup> It was also observed that the catalyst content and the polymerization conditions somehow influenced the rate of melt crystallization at  $T_c = 170$  °C. Sbirrazzuoli *et al.* investigated the non-isothermal crystallization kinetics of PEF obtained via the direct esterification process.

Similar structures of PEF crystals either formed from the glassy state or from the melt were observed via WAXS, but the growth dynamics were different. The Hoffman-Lauritzen theory described well the crystallization of PEF from the glassy state, but showed some deviations for PEF crystallized from the melt. A faster crystallization rate of crystals from the glassy state was found, which might be beneficial for PEF industrial production and processing.<sup>131</sup>

The mechanical analysis revealed that the Young's modulus and the maximum stress of PEF were 2070-2450 MPa and 35-67 MPa, respectively, which were comparable to those of PET (2000 MPa and 45 MPa, respectively).<sup>127</sup> Es *et al.* observed that PEF showed a brittle fracture behavior during the stress-strain test.<sup>129</sup> The elongation at break was 2.81 %, and much lower than that of PET (90-250 %). It might be the result of relatively lower molecular weight of PEF than PET. Dynamic mechanical thermal analysis (DMTA) performed on amorphous PEF showed that the storage modulus values ( $E'$ ) was in the range of 1.74 GPa to 2.28 GPa. When the temperature was above  $T_g$ , an obvious decrease in  $E'$  indicated the relatively poor mechanical properties. However, annealing was able to improve the mechanical properties above the  $T_g$ .<sup>129</sup>

Recently, a frequency dependent Arrhenius relationship was utilized to analyze the  $\beta$  relaxation of PEF and PET in order to investigate the macroscopic properties of the polymers.<sup>36</sup> From the  $\tan \delta$  curves, it was seen that the peak maximum of PEF pertaining to the  $\beta$  relaxation shifted to a higher temperature in comparison with PET, and the value decreased from 0.05 to 0.03. The shift was attributed to an increase in chain rigidity of PEF. Furthermore, the activation energy ( $E_A$ ) of the  $\beta$  relaxation of PEF and PET were  $68 \pm 2$  and  $72 \pm 1$  kJ/mol, respectively. Both phenyl ring-flipping and carbonyl motions were believed to contribute to the relaxation behavior in PET, but ring-flipping motion in PEF was inhibited due to the nonlinear axis of the furan ring rotation and the ring polarity (Fig. 4).

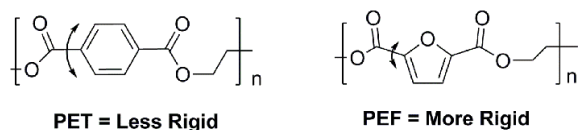


FIGURE 4 Polyester Performance Versus Ring-flipping<sup>36</sup>

Therefore, Koros *et al.* suggested that the carbonyl motions in PEF were more complex, and it might undergo some concerted motions with small scale furan ring oscillations.<sup>36</sup>

Studies on the thermal degradation kinetic and decomposition mechanism of PEF via pyrolysis-GC-MS (Py-GC/MS) showed that its decomposition occurred in two steps. The  $\beta$ -hydrogen bond scission dominated the decomposition process, producing vinyl compounds and carboxyl derivatives.<sup>132</sup> Moreover, a low amount of aldehydes and carbonyl compounds were detected as the products of  $\alpha$ -hydrogen bond scission and radical chain scission.

For the packaging applications, Koros *et al.* systematically investigated the sorption and the transport of carbon dioxide, water and oxygen in amorphous PEF.<sup>39,133-136</sup> The  $O_2$  sorption behavior of PEF was similar to PET at 35 °C, but it showed a significant reduction ( $\sim 11\times$ ) in oxygen permeability as compared to PET. The difference in oxygen permeability was mainly a result of a reduction in the chain mobility in PEF. In the case of  $CO_2$ , there were drastic reductions in permeability ( $19\times$ ) and diffusivity ( $31\times$ ) in PEF at 1 atm as compared to PET.<sup>133</sup> Kinetic and equilibrium sorption properties of PEF were also examined at 35 °C over the entire water activity range. PEF showed a higher equilibrium water uptake ( $\sim 1.8\times$ ) as compared to PET due to the higher affinity between water and polar furan ring. In addition, a significant reduction of the water diffusion coefficient for PEF was observed because of decreased segmental mobility of non-symmetrical furan ring. Finally, PEF exhibited an average permeability reduction of  $\sim 2.8\times$  for water as compared to PET at 35 °C.<sup>134,135</sup>

Taking recycling into consideration, both mechanical (re-extrusion) and chemical recycling (decomposition) are possible. An assessment of depolymerization products of FDCA based polyesters showed that hydrolysis or methanolysis catalyzed by a base, such as sodium methoxide and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), can recover dimethyl 2,5-furandicarboxylate and FDCA.<sup>137</sup> The methanolysis rate for PEF was much faster than that of PET. About 52 % of an initial PEF bar-shaped sample dissolved into methanol, while only 2 % of an original PET bar-shaped sample dissolved after a 90-minute test. In addition, when recycle streams of PET and PEF were mixed, the addition of up to 5 % (w/w) PEF showed no significant effect on the mechanical and physical properties of PET.<sup>38</sup>

#### *Poly(butylene-2,5-furandicarboxylate)*

Poly (butylene 2,5-furandicarboxylate) (PBF) prepared from FDCA and 1,4-butanediol has been widely investigated as well.<sup>138,139</sup> Gross *et al.* examined the effect of catalyst amounts, reaction time and temperature on the molecular weight and dispersity index (DI) of PBF. The polymerization process was a two-stage melt-polycondensation.<sup>140</sup> An increase in catalyst concentration (within a certain range) increased the molecular weight, and decreased the DI of PBF. Nevertheless, when the catalyst concentration reached 200 ppm, further increase in catalyst concentration showed less effect on them. In addition, the second-stage polymerization temperature was of importance for the final molecular weight of PBF. When the second-stage temperature was 200 °C, the  $M_w$  of PBF gradually increased during the extension of the reaction time from 2 to 8 h. However, a decrease in the  $M_w$  of PBF was observed when the second-stage reaction temperature was set to 220, 240 and 260 °C.

Zhou *et al.* have utilized a direct esterification method to prepare PBF.  $T_g$ ,  $T_m$  and  $T_d$  of PBF were



31 °C, 172.2 °C and 373 °C, respectively, which were lower than those of PBT.<sup>127</sup> The stress-strain curves revealed that Young's modulus, tensile strength and elongation at break were 1.1 GPa, 19.8 MPa and 2.8 %, respectively. The hydrophilicity of the polymeric matrix was confirmed by the result of the water contact angle test (84°).<sup>127</sup> Recently, Dubois *et al.* suggested that FDCA with high purity (99.9 %) facilitated the preparation of PBF with high  $M_w$ .<sup>141</sup> As a result, tensile modulus, strength and elongation at break were 1.9 GPa, 56 MPa and 256 %, respectively.

In contrast to only one transition at 172 °C ( $T_m$ ) mentioned above,<sup>127</sup> Ma *et al.* observed two different transitions of PBF using DSC at about 130 °C and 170 °C, respectively. The observation was similar to that of PBT (strained  $\beta$ -crystal, unstrained  $\alpha$ -crystal), indicating the possible presence of different crystallinities.<sup>138</sup> X-ray diffraction (XRD) analysis at different temperatures also revealed two transitions which occurred at 120 °C and 180 °C, respectively, which were consistent with the DSC results. Bikiaris *et al.* observed multiple melting behavior of PBF after isothermal crystallization from the melt in the DSC analysis.<sup>142</sup> However, only peaks of  $\alpha$ -crystal modification without  $\beta$ -crystal were observed in the WAXS results, and no crystal transition occurred on heating. Therefore, it was suggested that these multiple peaks in DSC might be the result of a recrystallization process.<sup>142</sup>

The effect of  $M_w$  on the thermal and mechanical properties of PBF was studied (Table 1).<sup>140</sup>  $T_g$  values of sample 3-6 were similar to that of PBT (40 °C). The presence of lower  $M_w$  species as plasticizers might have resulted in the relatively lower  $T_g$  for sample 1 and 2. Furthermore, the value of  $\Delta H_m$  decreased from 46 to 34 J/g when increasing  $M_w$  from  $16 \times 10^3$  to  $65 \times 10^3$  g/mol. The mobility of chains in PBF with low  $M_w$  increased, which was beneficial to the crystallization of polymers during cooling from melt. Furthermore, PBF samples with different  $M_w$  possessed similar spectra in the DMTA

analysis. There were two relaxation peaks in the  $\tan \delta$  plot at -74 °C and +39 °C, respectively. The micro-Brownian motion of polymer chains in the amorphous regions was responsible for the higher temperature peak, while another relaxation peak was mainly associated with the motion of butanediol groups and carbonyl residues in the non-crystalline phase. Results of the mechanical properties of PBF showed that the elongation at break and stress at break significantly increased when comparing sample 2-6 with sample 1. With a further increase in the  $M_w$  for samples 3 to 6, the values of the Young's modulus, elongation at break and stress at break were similar. When the  $M_w$  of the samples was too low, the lack of sufficient entanglements might have failed to provide satisfactory mechanical properties. Furthermore, samples with different percent crystallinity (from 8 to 44 %) were prepared by varying the annealing conditions for sample 6. The elongation at break significantly decreased from over 1000 to 7 % with the increase in the crystallinity, but it showed less effect on the Young's modulus and stress at break. It was suggested that when the amorphous phase was in the glassy state (below  $T_g$ ), the presence of crystallinity regions slightly influenced the variation of the modulus.

Solid-state  $^{13}\text{C}$  NMR was used to study the structure of PBF.<sup>138</sup> Five signals were shown in  $^{13}\text{C}$  cross-polarization magic angle spinning ( $^{13}\text{C}$  CP/MAS) NMR at 24.9, 65.8, 122.2, 147.8 and 159.0 ppm, respectively. However, the furan carbon signal at 122.2 ppm was split into two in  $^{13}\text{C}$  direct polarization magic angle spinning ( $^{13}\text{C}$  DP/MAS) NMR at 122.2 and 112.7 ppm, respectively. It was suggested that a carbon signal from the amorphous phase of polymers was able to be significantly augmented in  $^{13}\text{C}$  DP/MAS. Therefore, the results demonstrated the presence of furan rings in the crystalline and amorphous phases. In addition, it indicated that local phase changes could influence the chemical shifts of the furan carbon, instead of the carbons from butylene and ester. On the other hand, observations by polarized microscope showed that PBF retained the

TABLE 1 Thermal and Mechanical Parameters for PBF Determined by DSC and Tensile Testing as a Function of PBF Molecular Weight<sup>140</sup>

Sample no.	GPC Results		first heating	second heating		Young's Modulus (MPa)	Elongation at break (%)	Stress at break (MPa)
	$M_w \times 10^3$ (g/mol)	DI <sup>a</sup>	$T_g$ (°C) <sup>b</sup>	$\Delta H_m$ (J/g) <sup>c</sup>	$T_m$ (°C) <sup>c</sup>			
1	16	2.2	34	46	173	742±23	2.5±0.6	5.5±1.1
2	27	2.6	37	40	173	847±43	506±82	12.1±4.2
3	38	2.4	38	39	173	919±48	1184±28	29.3±1.5
4	49	2.3	39	38	172	969±64	1105±24	28.5±1.7
5	61	2.7	40	35	171	964±37	1108±108	32.9±5.2
6	65	2.8	39	34	172	959±58	1055±56	31.8±2.9

<sup>a</sup> DI equals to  $M_w/M_n$ . <sup>b</sup> Glass transition temperature determined from the first heating scan at 20 °C/min after quenching melted samples from liquid nitrogen. <sup>c</sup> Heat of fusion and melting temperatures determined from the second heating at 10 °C/min after cooling at 10 °C/min from the melt.

feature of PBT with fast crystallization, which is important for future commercial application. WAXS analysis revealed the crystal structure of PBF as triclinic crystal system.<sup>143</sup>

The thermal stability and decomposition kinetic of PBF were investigated via thermogravimetric analysis (TGA) together with Py-GC/MS.<sup>132</sup> The decomposition occurred in one step as compared to two steps for the PEF, and mainly via  $\beta$ -hydrogen bond scission. Furthermore, a low amount of aldehydes and radicals of 2-furancarboxyl and OH groups were detected, indicating the presence of  $\alpha$ -hydrogen bond and radical scission. The decomposition mechanism was quite similar to that of PBT.

### Copolyesters

Copolyesters from FDCA can be prepared by either incorporating more than one aliphatic diols or introducing other diacids monomers. Therefore, the properties of polymers, such as biodegradability, thermal, mechanical and barrier properties, are tunable, depending on the ratio and the structure of comonomer.<sup>144-147</sup> Preliminary results from the work of Gandini *et al.* showed that the thermal properties of poly(ethylene 2,5-furandicarboxylate-co-1,3-propylene-2,5-furandicarboxylate) (PEF-PPF)

were similar to PEF rather than PPF, even though there were 76 % of propylene moieties.<sup>70</sup> Additionally, Nie *et al.* studied the reactivity of ethylene glycol (EG) and 1,4-butanediol (BD) with FDCA, as well as the solubility of the corresponding copolyesters. <sup>1</sup>H NMR of PEF-PBF showed that the content of EG and BD was adjustable via changing the initial feed ratios. Moreover, BD showed a higher reactivity than EG in the polymerization process. PEF-PBF was difficult to dissolve in THF, toluene and chloroform but soluble in TFA, as well as slightly soluble in hot DMSO.<sup>148</sup>

Dubois *et al.* have prepared poly (butylene succinate-co-butylene furandicarboxylate) (PBS-PBF) via direct esterification and polycondensation.<sup>149</sup> The effect of mole percentage of FDCA ( $\delta F$ ) on the polymer yield, solubility, color, thermal and mechanical properties were studied.  $\delta F$  in the reaction system was able to influence the yield of polymer. When  $\delta F$  was less than 50 mol%, the reaction occurred following a two-step melt polycondensation procedure. However, when  $\delta F$  was in the range of 60-90 mol%, low  $M_w$  copolyesters were obtained under the same conditions. Both FDCA and succinic acid were able to catalyze the side reactions, such as the

formation of THF. FDCA has a stronger acidity than succinic acid. Therefore, the increase of  $\delta F$  could accelerate the side reactions leading to an incomplete esterification reaction. Several approaches have been proposed to resolve the issue, such as adding a tetrabutyl titanate (TBT) catalyst at the first stage together with an increase in diols/diacids ratio, lowering the esterification reaction temperature to suppress the side reactions, as well as using a TBT-La(acac)<sub>3</sub> mixture at the second stage to catalyze the polycondensation.<sup>149</sup> The solubility analysis indicated that the composition of PBS-PBF influenced the solubility of polymers in organic solvents. PBS-PBF with high  $\delta F$  (over 80 mol %) showed poor solubility in chloroform, heptane and methanol, but it was soluble in hot 1,1,2,2-tetrachloroethane at 50 °C. Fenouillot *et al.* exploited the biodegradation ability of PBS-PBF.<sup>150</sup> It showed that 90 % of copolyester could biodegrade within 180 days.

Ji *et al.* utilized adipic acid as a substitute for succinic acid to synthesize poly (butylene adipate-co-butylene furandicarboxylate) (PBA-PBF).<sup>151</sup>  $T_{d,5}$  and  $T_{d,max}$  of PBA-PBF were 342-388 °C and 417-430 °C, respectively. The effects of mole percentage of FDCA on  $T_g$ ,  $T_m$  and the mechanical properties are shown in Table 2. The  $T_g$  of copolyesters gradually increased with the increase in the mole percentage of FDCA, due to the stiffer chain conformation. The structure of PBA-PBF changed from semi-crystalline to amorphous, then to semi-crystalline according to the DSC and XRD results. It was suggested that the presence of adipate and furandicarboxylate units in a random way interrupted the crystallization of the chains (PBA-PBF30 to PBA-PBF50). The mechanical properties of PBA-PBF showed that the Young's modulus and tensile strength first decreased, and then increased, whereas the elongation at break followed the opposite trend. These properties were highly related to the variation in crystallinity of the copolymers. From the results of enzymatic degradation, it was observed that the introduction of small amounts of FDCA (below 10 mol%) was beneficial to the degradation of PBA-

PBF by lipase. The presence of FDCA decreased the crystallinity of PBA. However, furan units were eventually able to prevent the biodegradation of copolymers because of the rigidity of furan rings, as well as the overall high crystallinity.<sup>151</sup> Furthermore, Dubois *et al.* observed that the solubility of PBA-PBF was also composition-dependent.<sup>141</sup>

Poly (lactic acid) (PLA) has been widely utilized in the packaging and biomedical fields due to its biodegradability and biocompatibility.<sup>152</sup> Recently, PEF-PLA copolymers were obtained using Sb<sub>2</sub>O<sub>3</sub> as catalyst.<sup>153</sup> The  $M_w$  of copolyesters varied between 6900 and 9000 g/mol. Degradation experiments showed that PEF-PLA had an improved degradability in comparison with PEF. Moreover, high  $T_g$  and  $T_{d,5\%}$  values (76 and 324 °C, respectively) were observed after the incorporation of 8 mol% of lactyl units in PEF-PLA.<sup>153</sup> Cao *et al.* have synthesized PEF-PLA with higher  $M_w$  (68240 to 130433 g/mol) by two-stage condensation polymerization.<sup>154</sup> The  $T_g$  and  $T_{d,5\%}$  of PEF-PLA were adjustable depending on the molar ratio of PEF to PLA. Moreover, PEF-PLA were biodegradable in PBS solution and soil, which was evaluated by weight loss, molecular weight and structural changes, as well as SEM observation.

Copolyesters derived from terephthalic acid and FDCA have been synthesized in order to increase the bio-based content of PET.<sup>155</sup> The solubility of the copolyesters was poor. PET-PEF-4/1 (20 mol % furan) was semi-crystalline, and displayed similar thermal properties to PET in terms of  $T_g$  (62.4 °C),  $T_c$  (125 °C) and  $T_m$  (220 °C). The DMA analysis showed that the  $\beta$  and  $\alpha$  transition temperatures of PET-PEF-4/1 were -40.9 and 67.5 °C, respectively, which were closed to those of PET (-58.3 and 103.2 °C, respectively).

Table 3 summarizes the molecular weights and partial thermal properties of FDCA-based (co)polyesters. Generally, the  $T_g$  and  $T_m$  of FDCA-based polyesters gradually decreased with the increase in the methylene units of aliphatic linear diols (from 2 to 18). Polyesters were thermally stable up to 300 °C. Additionally, the

TABLE 2 Glass Transition Temperature ( $T_g$ ), Melting Temperature ( $T_m$ ), Young's Modulus ( $E$ ), Tensile Strength ( $\sigma_{max}$ ) and Elongation at Break ( $\epsilon_{max}$ ) of PBA, PBF and PBA-PBF Copolyesters<sup>151</sup>

Samples	$T_g$ (°C)	$T_m$ (°C)	$E$ (MPa)	$\sigma_{max}$ (MPa)	$\epsilon_{max}$ (%)
PBA	- <sup>a</sup>	55	168 ± 3.0	15 ± 1.2	463 ± 37
PBA-PBF10	- <sup>a</sup>	49	110 ± 10	12 ± 1.0	755 ± 64
PBA-PBF20	-44	30	55 ± 5.1	11 ± 1.1	976 ± 53
PBA-PBF30	-37	- <sup>c</sup>	0.14 ± 0.03	2.6 ± 0.08	1850 ± 183
PBA-PBF40	-28	- <sup>c</sup>	1.5 ± 0.4	19 ± 1.3	1521 ± 93
PBA-PBF50	-19.7	- <sup>c</sup>	10 ± 0.7	20 ± 0.9	1040 ± 56
PBA-PBF75	0 <sup>b</sup>	134	76 ± 4.2	30 ± 1.6	425 ± 23
PBF	36	171	875 ± 18	35 ± 2.6	55 ± 10

<sup>a</sup> Not measured due to instrumental limitation. <sup>b</sup> Estimated from DSC analysis of PBA-PBF75 during second heating at 10°C/min. <sup>c</sup> No  $T_m$  was observed

TABLE 3 Molecular Weight ( $M_n$ ), Glass Transition Temperature ( $T_g$ ), Melting Temperature ( $T_m$ ) and Decomposition Temperature ( $T_d$ ) of (Co) polyesters.

(Co)polyester	Diols (and Diacids)	$M_n \cdot 10^3/g \text{ mol}^{-1}$	$T_g/^\circ\text{C}$	$T_m/^\circ\text{C}$	$T_d/^\circ\text{C}$	Ref
PEF	Ethylene Glycol	18-44	75-80	210-215	389-398	38,70,126
PPF	1,3-Propanediol	15-23	50-58	170-180	375-390	38,70,156
PBF	1,4-Butanediol	23-26	30-45	167-172	329-388	38,138
PBF2	2,3-Butanediol	2-13	71-113	-	276-301	157
PHF	1,6-Hexanediol	13-23	7-28	145	350-390	38,158
PDPF	2,2-Dimethyl-1,3-Propanediol	15	68	198	408	159
POF	1,8-Octanediol	20-34	-5-22	140-148	375-400	160
PDeF	1,10-Decanediol	36	1	112-116	340-359	161
PDF	1,12-Dodecanediol	25	-	108	340	132,162
PODF	1,18-Octadecanediol	22	-	97	-	162
PDAF	D-Isosorbide	9-25	173-194	-	350 <sup>d</sup>	70
PDAMF	D-Isomannide	14-20	187-191	-	-	163
PDAIF	D-Isoidide	5-21	140-196	-	275 <sup>d</sup>	70
PXIF	Isoidide-2,5-dimethanol	30	94	250	376 <sup>a</sup> ; 411 <sup>c</sup>	164
PBDMF	1,4-Benzenedimethanol	22	87	-	300 <sup>d</sup> ; 390 <sup>b</sup>	70
PEF-PPF	Ethylene glycol and Propanediol	14	80	215	398	70
PEF-PBF	Butanediol, Ethylene Glycol	26-58	39-71	127-163	334-341	148
PBS-PEF	Ethylene Glycol, Succinic Acid	25-57	-	21-172	378-438	165
PBS-PBF	Butanediol, Succinic acid	58-61	-25 to 30	54-159	339-350 <sup>a</sup>	149,150
PBA-PBF	Adipic acid, Butanediol	28-57	-44 to 36	30-171	-	151
PET-PEF	Ethylene Glycol, Terephthalic acid	6-16	62-75	198-220	385-408 <sup>b</sup>	155
PEF-PLA	Ethylene Glycol, Lactic acid	68-130	25-79	119	232-324 <sup>a</sup>	153,154
PBF-PBD	1,4-Butanediol, Diglycolic acid	-	6-35	106-164	366-388 <sup>b</sup>	166

<sup>a</sup> Decomposition at 5% weight loss. <sup>b</sup> Maximum degradation temperature. <sup>c</sup> Decomposition temperature at the maximum weight-loss rate. <sup>d</sup> Onset of thermal decompositions.

incorporation of methyl groups as the side chain of polymers increased the  $T_g$ , such as the  $T_g$  of polymer synthesized from 2,3-butanediol (71-113 °C) and ethylene glycol (75-80 °C).

#### Other FDCA Based Polymers

FDCA and its derivatives have been used to prepare other polymers or resins,<sup>167,168</sup> such as polyamides,<sup>169,170</sup> thermotropic polyesters,<sup>171,172</sup> photodegraded polyesters,<sup>173</sup> branched furanic polyester resins,<sup>174</sup> linear and cross-linked poly(ester amide),<sup>88,175</sup> epoxy resins<sup>74</sup> and poly(ester urethanes).<sup>168</sup> For polyamides,<sup>71,99,169</sup>

Gandini *et al.* synthesized and characterized polyamides from FDCA and aromatic diamines.<sup>99</sup> These furanic-aromatic polyamides displayed a regular structure, high molecular weight and good thermal stability. Cureton *et al.* synthesized polyamides from FDCA and *p*-phenylenediamine by direct polycondensation and interfacial polymerization, respectively.<sup>176</sup> It was observed that interfacial polymerization was a more suitable synthesis method in terms of the obtained molecular weight and polydispersity index. As bio-based Kevlar analogs, FDCA based polyamides showed good chemical resistance in most organic solvents, as well as improved solubility. Moreover, these polyamides were fully amorphous polymers with a high  $T_g$  ( $> 180$  °C) and satisfactory thermal stability (nearly 400 °C). The fully amorphous structure was unexpected, since the occurrence of crystallization in other furan polyamides has been observed using aliphatic diamines as the monomer.<sup>162</sup> Therefore, the use of aromatic diamine (*p*-phenylenediamine) might be the reason for the amorphous nature of the polymer due to its more rigid structure, preventing the formation of intermolecular hydrogen bonding. Zhu *et al.* have recently synthesized a series of aromatic furanic polyamides from FDCA and various aromatic diamines by direct polycondensation under optimized conditions. No  $T_m$  was observed from DSC analysis, indicating the amorphous structure of these polyamides. In addition, it was suggested that the thermal and mechanical properties of materials varied with different polymer structures.<sup>177</sup>

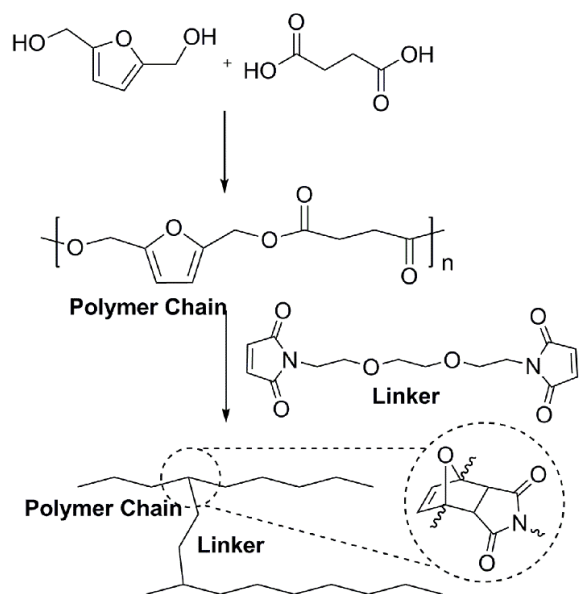
A molecular dynamic simulation test was performed to further analyze FDCA based polyamides. The results for this test showed that compared to nylons, furan polyamides exhibited higher van der Waals cohesive energy densities. Moreover, furan polyamides maintained more rigid planar structures near furan rings. Therefore, FDCA based polyamides showed a higher  $T_g$  and comparable mechanical properties than those of nylons, although the overall intermolecular hydrogen bonding in furan

polyamides was weaker than that in nylons.<sup>169</sup> On the other hand, Rastogi *et al.* investigated the effect of the 2,5-furandicarboxamide moiety on the formation of hydrogen bonding in poly(ester amide)s. It was suggested that the relatively weak hydrogen bonding in furan polyamides was due to the presence of oxygen atom in FDCA which functioned as a hydrogen bonding acceptor, forming the intramolecular hydrogen bonding with the amide hydrogens. Therefore, it prevented the formation of intermolecular hydrogen bonding.<sup>175</sup>

In summary, FDCA based polyesters (PEF and PBF) have been systematically investigated in terms of thermal, mechanical and barrier properties. The rigidity of furan rings was one of the key features to impart the comparable properties of furan based polymers as compared to petroleum-based analogues. However, challenges still exist to synthesize polymers with high molecular weights from FDCA in order to avoid the decarboxylation and color issues. Therefore, the development of an efficient catalyst system with relatively mild reaction condition seems to be necessary for the synthesis of FDCA based polymers. On the other hand, synthesis of copolymers containing FDCA provided opportunities to adjust the thermal and mechanical properties, as well as degradability. Therefore, research studies on the synthesis and characterization of copolymer from FDCA are still needed, particularly utilizing other renewable resources or monomers with extra functionality.

### ***Polymers from BHF and Its Derivatives***

BHF, a derivative of HMF, has shown potential as an interesting diol in the preparation of polyesters, polyurethanes and thermosetting polymers. Importantly, further Diels-Alder reaction on the furan ring imparted the possibility of preparing functional polymers. Yoshie *et al.* have reported BHF based polyesters with self-healing ability via a reversible Diels-Alder reaction between the furan and maleimide groups (Scheme 2).<sup>178</sup> The  $T_g$  of polyesters increased from 1.8 to 9.6 °C as the molar ratio of



SCHEME 2 Synthesis of Self-healing Polyesters.

crosslinkers to linear polyesters increased from 1:10 to 1:2. Moreover, the mechanical properties of the polymers could be adjusted by controlling the amounts of crosslinkers. When the ratio of crosslinker to polyester was 1:2, the Young's modulus, ultimate strength and elongation at break of the resulting crosslinked polymers were around 1230 MPa, 19.2 MPa and 101 %, respectively.<sup>50</sup> The choice of bis-maleimides crosslinkers was a key factor for designing these self-healing polymers. Bis-maleimides with flexible and long segments were beneficial to self-healing properties, while short and rigid crosslinkers reduced the efficiency of self-healing behavior.<sup>178</sup> Interestingly, polymer films with multi-shape memory features could be synthesized by changing the  $T_g$  of polymers as mentioned above.<sup>179</sup> BHF has also been exploited to prepare copolymers with 1,4-butanediol and succinic acid. A network was generated after crosslinking the copolymers by the Diels-Alder reaction. The thermal and mechanical properties of the copolymers were highly associated with the monomer composition and the maleimide/furan ratio in the polymers.<sup>180</sup> Recently, a derivative of BHF was synthesized for the thiol-Michael addition reaction.<sup>181</sup> The use of dimethylphenylphosphine catalyst had several

advantages including short reaction times, mild reaction temperature and high yield. As a result, a bio-based furan polymer with relatively high molecular weight (19,529 g/mol) was synthesized within 15 mins. The synthesis of a reversible organogel further indicated that these polymers can be a starting point for engineering different materials using the Diels-Alder reaction.<sup>181</sup>

On the other hand, Du Prez *et al.* prepared BHF based polyurethane foams with additional surface functionalities through the Diels-Alder reaction.<sup>51</sup> More than 90 % of the furan groups reacted after 20 h with a nine-fold excess of N-methylmaleimide. The Retro-Diels-Alder reaction was performed by refluxing polyurethane foams in water at 100 °C for 24 h. However, the reversibility of the Diels-Alder reaction might limit the application of polyurethane foams at high temperature.<sup>51</sup>

Recently, 2,5-bis[(oxiranylmethoxy)methyl]-furan (BOF) was synthesized as a renewable monomer for epoxy resin. The thermomechanical properties of the resins were evaluated in comparison to those of 2,5-bis[(2-oxiranylmethoxy)methyl]-benzene (BOB).<sup>78</sup> BOF monomers were liquids of low viscosity. The  $T_g$  and storage modulus of BOF-based resins were of higher values than those of BOB-based resins. The rigidity of the furan rings, as well as enhanced hydrogen bonding between the hydroxyl groups generated during the curing process and the oxygen atoms in the furan rings, might have contributed to those results. Furthermore, additional methylene units between the aromatic rings and the glycidyoxy groups in BOF and BOB monomers decreased the  $T_g$  of the resins due to lesser constraint of the aromatic rings.<sup>78</sup> Recently, the same group of authors prepared fully renewable thermosetting polymers from BOF with 5,5'-methylenedifurfurylamine (DFDA) and 5,5'-ethylidenedifurfurylamine ( $\text{CH}_3\text{DFDA}$ ) as amine curing agents. The thermosets showed a  $T_g$  value above 60 °C. The storage modulus value at room temperature was 3.5 GPa and the thermal

stability was up to 272 °C (5 wt % loss).<sup>79</sup> More recently, the effects of the furan rings on the thermomechanical properties of BHF based epoxy resins were investigated by molecular simulation.<sup>182</sup> It was suggested that the high packing density from the strong polarity in BOF based resins, rather than enhanced hydrogen bonding mentioned above, reduced the mobility of the polymer chains.

### **Polymers from DFF**

Despite growing interest in the preparation of DFF from either HMF or other natural resources,<sup>183-185</sup> examples of DFF based polymers are relatively rare.<sup>76,186-188</sup> A crystalline polymer resin was obtained via condensation of DFF with urea at 110 °C.<sup>189</sup> NMR analysis showed that one aldehyde group of DFF can condense with two urea molecules. The resins were insoluble in water and common organic solvents, but slightly soluble in DMSO and DMF at 45 °C. Swelling experiments showed that the degree of swelling was 12 % after equilibrium, indicating the presence of crosslinking. Schiff based polymers have also been synthesized by polymerization of DFF with aromatic or aliphatic diamines.<sup>190</sup> NMR and mass spectra analysis indicated that the reaction proceeded quickly to form imine bonds. A regular chain structure was confirmed through <sup>13</sup>C CP/MAS NMR. In addition, DFF-based porous organic frameworks (DPOF) were prepared by condensation of DFF with aromatic diamines.<sup>186</sup> These polymers were insoluble in water and common organic solvents. TGA analysis revealed that the thermal stability was up to 300 °C under N<sub>2</sub>. The geometry of the monomers significantly influenced the crystal and porous morphology of the polymers. Condensation of DFF with nonlinear diamines led to an amorphous structure, while the crystalline structure in DPOF formed using linear diamines. The porous properties of DPOF were analyzed by nitrogen adsorption/desorption, and the pore size distribution was calculated from the non-local density functional theory model. Both micropores and mesopores were present in DPOF. The rigidity and contortion of the

molecular structure limited space-efficient packing of polymers in the solid state, leading to the porous structure. In the case of DPOF prepared from DFF and m-phenylenediamine (DFP), specific surface area determined by the Brunauer-Emmett-Teller (BET) technique and pore volume were 830 m<sup>2</sup>/g and 2.10 cm<sup>3</sup>/g, respectively. The capacity of adsorption of CO<sub>2</sub> associated with gas storage was 77.0 mg/g.<sup>186</sup>

### **CONCLUSIONS**

Although a variety of furan based monomers are available, the efficient, simple and inexpensive production of these valuable monomers from renewable resources is desired. Continuous efforts to exploit novel derivatives from HMF are necessary in order to generate new polymers for broader applications, especially in combination with other polymerization methods, such as click, radical and photo polymerization.<sup>181</sup> On the other hand, the advantages of the furan rings in the polymers lie in their ability to improve the mechanical properties and thermal stability. Therefore, the introduction of furan rings into other bio-based polymers seems to be a promising route to adjust the properties of the polymers. Additionally, the incorporation of other functional monomers to synthesize copolymers or the preparation of composites provide the opportunity to tune the thermal and mechanical properties of materials from bio-based HMF and its derivatives. Finally, enzymatic catalysis is worthy of investigation due to the mild reaction conditions, environmental friendliness and high tolerance toward functional groups.<sup>191-198</sup>

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## GRAPHICAL ABSTRACT

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Advances in polymer precursors and bio-based polymers synthesized from 5-hydroxymethylfurfural

The production of polymers from petroleum-based chemicals has caused serious sustainability concerns, thereby stimulating the development of bio-based polymers. 5-Hydroxymethylfurfural as an important platform chemical provides such an opportunity to synthesize varieties of interesting and useful polymers. This review highlights the research studies that have been conducted in the synthesis of HMF derivatives, and polymers derived from HMF or derivatives of HMF. Moreover, the potential opportunity to this field has also been suggested.

## GRAPHICAL ABSTRACT FIGURE

